

## Method for producing paper, paperboard and cardboard

5 The present invention relates to a process for the production of paper, board and cardboard by adding uncrosslinked organic microparticles and at least one retention aid to the paper stock and draining the paper stock over a wire.

10 Inorganic microparticles, such as bentonite or colloidal silica sols, are used in the production of paper together with cationic polymers for improving the retention and the drainage of the paper stock, cf. EP-A-0 235 893, EP-A-0 335 575, EP-A-0 310 959, US-A-4 388 150 and WO-A-94/05595. In this process, a cationic polymer is metered in an amount of more than 0.03% by weight, based on dry paper stock, the mixture is then subjected to the action of a shear field, the initially formed flocks being broken up into microflocks, bentonite or silica is then added and the pulp thus obtained is drained without further action of shear forces. According to the process of DE-A-102 36 252, a  
15 microparticle system comprising a cationic polymer and a finely divided inorganic component is metered to the paper stock after the final shear stage upstream of the headbox and the paper stock is then drained. Compared with the use of cationic polymers alone as retention aids, papers having an improved formation are obtained using the multicomponent systems comprising cationic polymers and inorganic  
20 microparticles.

EP-A-0 462 365 discloses organic microparticles which may be uncrosslinked or crosslinked and which in each case comprise at least 1, but generally at least 5, % by weight of an ionic comonomer incorporated in the form of polymerized units. The  
25 particle size of the uncrosslinked, water-insoluble microparticles is below 60 nm, while that for the crosslinked microparticles is less than 750 nm. The organic microparticles are used in papermaking together with a high molecular weight ionic polymer as a retention aid. In addition to the organic microparticles, bentonite or finely divided silica may also be used in papermaking. Suitable high molecular weight polymers are both  
30 synthetic organic polymers and polysaccharides.

EP-A-0 810 274 discloses binders based on aqueous styrene/acrylate polymer dispersions having a mean film formation temperature of less than 10°C. The polymers can, if appropriate, comprise up to 1% by weight of a monomer comprising acid groups.  
35 The particle size of the disperse polymer particles is preferably in the range from 100 to 300 nm. The binders are used, for example, for the preparation of coating materials, such as plastics dispersion renders, tile adhesives, coating materials and in particular low-emission emulsion paints.

40 WO-A-02/101145 discloses aqueous mixtures which comprise anionic, crosslinked, polymeric particles having a particle size in the unswollen state of less than 750 nm, in particular from 25 to 300 nm, and colloidal anionic silica particles. The mixtures are used in papermaking together with a cationic polymer as drainage and retention aids.

However, they can also be used as flocculants and for treating wastewater and sludges.

5 Further microparticle systems which are used as an additive to the paper stock in papermaking are disclosed in EP-A-0 497 030 and EP-A-0 0635 602. US-A-6 083 997 discloses the preparation of an anionic nanocomposite which is used as a retention aid and drainage aid in papermaking. As is evident therefrom, waterglass is mixed with an anionic polyelectrolyte based on polysulfonates, polyacrylates or polyphosphates and either silica is added or the silica is produced in situ.

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It is an object of the present invention to provide a further process for the production of paper, board and cardboard using a microparticle system.

15 We have found that this object is achieved, according to the invention, by a process for the production of paper, board and cardboard by adding ionic, water-insoluble, uncrosslinked, organic microparticles and at least one retention aid to a paper stock and draining the paper stock over a wire, if the organic microparticles used are water-insoluble, uncrosslinked, organic polymers having an average particle size of less than 500 nm and a content of polymerized ionic monomers of less than 1% by weight or  
20 water-insoluble, uncrosslinked, organic microparticles having an average particle size of less than 500 nm and a content of polymerized ionic monomers of not more than 10% by weight, which are obtainable by polymerizing the monomers in the presence of silica, waterglass, bentonite and/or mixtures thereof.

25 Said particle sizes are always the weight average particle sizes  $d_{50}$ . Said particle size was determined by dynamic light scattering on a 0.01% strength by weight dispersion at 23°C by means of an  $\text{lic}$  autosizer from Malvern Instruments, UK. The average particle size of the water-insoluble, uncrosslinked, organic polymers is preferably from 10 to 100 nm and the content of polymerized ionic monomers is from 0.1 to 0.95% by  
30 weight. Microparticles having average particle sizes of the water-insoluble, uncrosslinked, organic polymers of from 10 to 80 nm and a content of polymerized ionic monomers of from 0.2 to 0.7% by weight are particularly preferred. In general, the average particle size of the microparticles is in the range from 15 to 50 nm.

35 The microparticles comprising water-insoluble, uncrosslinked, organic polymers comprise either at least one anionic monomer or one cationic monomer incorporated in the form of polymerized units. Aqueous dispersions which comprise anionic microparticles are disclosed in EP-A-0 810 274, page 3, line 3 to page 15, line 59, disclosed in connection with the prior art. Suitable water-insoluble, uncrosslinked,  
40 organic polymers which carry an ionic charge are obtainable, for example, by free radical aqueous emulsion polymerization of a monomer mixture comprising

- (a) from 30 to 55 parts by weight of at least one monomer whose homopolymer has a glass transition temperature  $T_g$  of  $<20^\circ\text{C}$ ,
- (b) from 45 to 70 parts by weight of at least one monomer whose homopolymer has a glass transition temperature  $T_g$  of  $>50^\circ\text{C}$  and
- 5 (c) from 0.01 to less than 1 part by weight of a monomer having ionic groups,

the sum of the parts by weight of (a) and (b) always being 100. The monomers having ionic groups can impart to the polymer either an anionic charge, if, for example, monoethylenically unsaturated monomers having acidic groups are used in the  
 10 polymerization, or a cationic charge, if the polymerization is carried out in the presence of monoethylenically unsaturated, basic monomers. The glass transition temperature  $T_g$  is understood as meaning the limit of the glass transition temperature to which said glass transition temperature tends with increasing molecular weight, according to  
 15 G. Kanig (cf. *Kolloid-Zeitschrift & Zeitschrift für Polymere*, Volume 190, page 1, equation 1). It is determined by the DSC method (differential scanning calorimetry, 20 K/min, midpoint). The  $T_g$  values for the homopolymers of most monomers are known, cf. for example Ullmann's Encyclopedia of Industrial Chemistry, Verlag Chemie Weinheim, 1992, Part 5, Vol. A21, page 169.

20 The monomer (a) is, for example, selected from at least one  $\text{C}_1$ - to  $\text{C}_{10}$ -alkyl acrylate,  $\text{C}_5$ - to  $\text{C}_{10}$ -alkyl methacrylate,  $\text{C}_5$ - to  $\text{C}_{10}$ -cycloalkyl (meth)acrylate,  $\text{C}_1$ - to  $\text{C}_{10}$ -dialkyl maleate and/or  $\text{C}_1$ - to  $\text{C}_{10}$ -dialkyl fumarate. Typical monomers (b) are, for example, selected from at least one vinylaromatic monomer and/or one  $\alpha,\beta$ -unsaturated carbonitrile or carbodinitrile.

25  $\text{C}_1$ - to  $\text{C}_n$ -alkyl groups are to be understood as meaning linear or branched alkyl radicals of 1 to n carbon atoms, e.g. methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, n-hexyl, 2-ethylhexyl, n-octyl, isooctyl and n-decyl.  $\text{C}_5$ - to  $\text{C}_{10}$ -Cycloalkyl groups are, for example, cyclopentyl, cyclohexyl or cyclooctyl, which may  
 30 optionally be substituted in each case by 1, 2 or 3 alkyl groups of 1 to 4 carbon atoms.

The water-insoluble, uncrosslinked, organic polymer is preferably composed of

from 35 to 50 parts by weight of monomer units (a),  
 35 from 50 to 65 parts by weight of monomer units (b) and  
 from 0.01 to 0.95 part by weight of monomer units (c),

the sum of the monomer units (a) and (b) always being 100.

40 Where it is an anionic monomer, the monomer (c) is, for example, selected from  $\alpha,\beta$ -unsaturated  $\text{C}_3$ - to  $\text{C}_6$ -carboxylic acids,  $\alpha,\beta$ -unsaturated  $\text{C}_4$ - to  $\text{C}_8$ -dicarboxylic acids, anhydrides thereof, monoethylenically unsaturated alkanesulfonic acids,

- monoethylenically unsaturated phosphonic acids and/or monoethylenically unsaturated arylsulfonic acids. The monomer (c) may be used in the polymerization if appropriate in a form partly or completely neutralized with alkali metal, alkaline earth metal and/or ammonium bases. Moreover, it is possible for polymers which comprise the monomers (c) incorporated by polymerization in the form of the free acid groups to be neutralized during or after the end of the polymerization. Suitable bases are, for example, sodium hydroxide solution, potassium hydroxide solution, sodium carbonate, potassium carbonate, sodium bicarbonate, ammonia, amines, such as trimethylamine, propylamine or butylamine, pyridine, piperidine, morpholine and alkanolamines, such as monoethanolamine, diethanolamine and triethanolamine, calcium oxide, calcium hydroxide, magnesium oxide and magnesium hydroxide. Preferred monomers of group (c) are acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, maleic anhydride, itaconic acid, itaconic anhydride, vinylsulfonic acid, methallylsulfonic acid, vinylbenzenesulfonic acid, acrylamidoethanesulfonic acid, acrylamido-2-methylpropanesulfonic acid, 2-sulfoethyl (meth)acrylate and sulfopropyl (meth)acrylate. Particularly preferred monomers of this group are acrylic acid, methacrylic acid and acrylamido-2-methylpropanesulfonic acid, mixtures of these monomers and alkali metal and ammonium salts thereof, in particular sodium salts thereof.
- If the monomer (c) is a cationic monomer, this is to be understood as meaning, for example, the following monomers: diallyldimethylammonium chloride, di-C<sub>1</sub>-to C<sub>2</sub>-alkylamino-C<sub>2</sub>- to C<sub>4</sub>-alkyl (meth)acrylates and di-C<sub>1</sub>- to C<sub>2</sub>-alkylamino-C<sub>2</sub>- to C<sub>4</sub>-alkyl(meth)acrylamides. Said dialkylaminoalkyl (meth)acrylates and dialkylaminoalkyl(meth)acrylamides are preferably used in the form of salts with mineral acids or organic acids or in quaternized form. The quaternizing agent used is, for example, methyl chloride, ethyl chloride or dimethyl sulfate. Examples of preferably used cationic monomers are diallyldimethylammonium chloride and the following salts of sulfuric acid or hydrochloric acid or compounds quaternized with methyl chloride: dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, dimethylaminopropyl methacrylate, dimethylaminoethylmethacrylamide and dimethylaminopropyl(meth)acrylamide. The polymers may also comprise, as cationic groups, vinylamine units in the form of salts with mineral acids or in quaternized form. Polymers having such groups are obtained, for example, if the polymerization is carried out in the presence of vinylformamide as a comonomer, and the vinylformamide units present in the copolymer are then hydrolyzed with sulfuric acid to give vinylamine units.

- Monomers of group (c) are present in an amount of less than 1 part by weight, based on 100 parts by weight of the sum of the monomers (a) and (b), in the monomer mixture which is subjected to the polymerization. Preferably, the monomer mixture comprises from 0.01 to 0.95, in particular from 0.2 to 0.7, part by weight, based on 100 parts by weight of the monomer (a) and (b), of at least one monomer (c).

- In addition to said polymers of the components (a), (b) and (c), those microparticles of water-insoluble, uncrosslinked, organic polymers having an average particle size of less than 500 nm and a content of polymerized ionic monomers of up to 10% by weight which are obtainable by polymerizing the monomers on which these polymers are based in the presence of silica, waterglass, bentonite and/or mixtures thereof are also suitable for papermaking. In the case of this type of microparticles, the content of monomers of group (c) is, for example, from 0.1 to 10, preferably from 1.5 to 7, in particular from 2 to 5, % by weight.
- 10 Examples of monomers (a) are vinyl ethers of C<sub>3</sub>- to C<sub>10</sub>-alkanols, branched and straight-chain C<sub>3</sub>- to C<sub>10</sub>-olefins, C<sub>1</sub>- to C<sub>10</sub>-alkyl acrylates, C<sub>5</sub>- to C<sub>10</sub>-alkyl methacrylates, C<sub>5</sub>- to C<sub>10</sub>-cycloalkyl (meth)acrylates, C<sub>1</sub>- to C<sub>10</sub>-dialkyl maleates and/or C<sub>1</sub>- to C<sub>10</sub>-dialkyl fumarates. Particularly preferred monomers of this group are, for example, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, di-n-butyl maleate and/or di-n-butyl fumarate.

- Examples of suitable monomers (b) are vinylaromatic monomers, such as styrene or  $\alpha$ -methylstyrene, and styrene or  $\alpha$ -methylstyrene substituted by 1, 2 or 3 C<sub>1</sub>- to C<sub>4</sub>-alkyl groups, chlorine and/or methoxy groups. Preferred monomers of group (b) have a glass transition temperature above 80°C. Examples of these are styrene,  $\alpha$ -methylstyrene, o- or p-vinyltoluene, acrylonitrile, methacrylonitrile, maleodinitrile, fumarodinitrile or mixtures thereof.

- 25 The copolymers may if appropriate comprise further monoethylenically unsaturated monomers, such as acrylamide, methacrylamide, N-vinylpyrrolidone and N-vinylcaprolactam, incorporated in the form of polymerized units. The amounts are, for example, from 0 to 10 parts by weight, based on 100 parts by weight of the monomers (a) and (b).

- 30 The polymerization of the monomers is effected by the known methods of emulsion polymerization in the presence of initiators which form free radicals under the polymerization conditions, such as peroxides, hydroperoxides, azo compounds or redox initiators, and in the presence of emulsifiers. Further information in this context can be obtained from the abovementioned EP-A-0 810 274, pages 4 and 5. The polymerization of the suitable monomers can, however, also be carried out in the presence of silica, waterglass, bentonite and/or mixtures thereof. Aqueous dispersions of ionic, water-insoluble, uncrosslinked, organic polymers having an average particle size below 500 nm are obtained. The polymerization can, however, also be effected by preparing an emulsion from water, the monomers, a hydrocarbon which is liquid at room temperature, such as hexane, pentane, isooctane, toluene and/or xylene, and at

least one surfactant and polymerizing the monomers in the presence of free radical initiators.

Preferred polymers are those which comprise

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- (a) at least one monomer from the group consisting of n-butylacrylate, isobutyl acrylate, n-propyl acrylate, isopropyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate and methyl acrylate,
- (b) at least one monomer from the group consisting of styrene,  $\alpha$ -methylstyrene, acrylonitrile and methacrylonitrile and
- 10 (c) at least one monomer from the group consisting of acrylic acid, methacrylic acid, maleic acid and acrylamido-2-methylpropanesulfonic acid

in the abovementioned amounts, incorporated in the form of polymerized units.

- 15 Copolymers which comprise, incorporated in the form of polymerized units n-butyl acrylate and styrene in the weight ratio of 1 : 1 and from 0.2 to 0.7% by weight of methacrylic acid or acrylic acid are particularly preferred.

- 20 The average molar mass  $M_w$  of the polymers is, for example, from 500 000 to 5 million, preferably from 1 to 3 million.

- 25 The ionic, water-insoluble, uncrosslinked, organic microparticles described above are added together with at least one retention aid to the paper stock in papermaking. The organic microparticles promote the action of the retention aid. The organic microparticles are used, for example, in amounts of from 0.1 to 1, preferably in amounts of from 0.2 to 0.6, % by weight, based on dry paper stock. The amounts of retention aid are, for example, from 0.01 to 0.09, preferably from 0.02 to 0.04, % by weight, based on dry paper stock. Retention aids which may be used are all conventional polymers which are known for this purpose, for example polyacrylamides,
- 30 cationic polyacrylamides, such as copolymers of acrylamide and dimethylaminoethyl acrylate which is quaternized with methyl chloride, polyvinylamines, polydiallyldimethylammonium chlorides, anionic polyacrylamides, such as copolymers of acrylamide and acrylic acid or copolymers of acrylamide and methacrylic acid, and also polydialkylaminoalkyl(meth)acrylamides, such as polydimethylaminoethyl-
- 35 acrylamide and polydimethylaminoethylmethacrylamide, which in each case are used in protonated or in quaternized form, and polyethylene oxides, which if appropriate may be cationically and/or anionically modified. Furthermore, polyamidoamines which are grafted with ethylenimine and crosslinked with dichlorohydrin ethers of polyethylene glycols are suitable as retention aids. Further conventional retention aids are cationic
- 40 starches. Such starches are prepared, for example, by reacting starch with cationizing agents, such as 3-chloro-2-hydroxypropyltrimethylammonium chloride. The degree of substitution of the cationic starch is, for example from 0.01 to 1, preferably from 0.02 to

0.5. Amphoteric starches may also be used as retention aids provided that they have an excess cationic charge. The retention aids are known to have a high molecular weight and thus differ substantially from fixing agents which are based on the same monomers. The molecular weight  $M_w$  of the retention aids is, for example, at least 500 000, preferably >1 million, generally >2 million, in particular >5 million.

According to the novel process, all paper qualities can be produced, for example cardboard, single-ply/multiply cardboard for folding cartons, single-ply/multiply liners, corrugated material, newsprint, so-called medium-ply writing and printing papers, natural gravure printing paper and light-weight coating papers. In order to produce these papers, it is possible to start, for example, from groundwood, thermomechanical pulp (TMP), chemothermomechanical pulp (CTMP), pressure groundwood (PGW), wood pulp and sulfite and sulfate pulp. The chemical pulps may be either short-fiber or long-fiber. According to the novel process, wood-free qualities, which give highly white paper products, are preferably produced.

The papers can if appropriate comprise up to 40, in general from 5 to 35, % by weight of fillers. Suitable fillers are, for example, titanium dioxide, natural and precipitated chalk, talc, kaolin, satin white, calcium sulfate, barium sulfate, clay and/or alumina.

Paper can also be produced in the presence of conventional process chemicals. For example, at least one fixing agent, strength agent for paper and/or an engine size can also be added to the paper stock. Suitable fixing agents are, for example, polymers comprising vinylamine units, polydiallyldimethylammonium chloride, polyethylenimines, polyalkylenepolyamines and/or dicyandiamide polymers. The molecular weight  $M_w$  of the fixing agent is, for example, up to 300 000, in general in the range from 50 000 to 1 million.

According to the invention, water-insoluble, uncrosslinked, organic polymers having an average particle size of less than 500 nm and a content of polymerized ionic monomers of less than 1% by weight are metered together with at least one cationic, anionic, amphoteric or neutral synthetic organic polymer and/or cationic starch as a retention aid to the paper stock before the final shear stage upstream of the headbox. In an embodiment of the novel process, water-insoluble, uncrosslinked, organic polymers having an average particle size of less than 500 nm and a content of polymerized ionic monomers of less than 1% by weight are metered together with at least one retention aid and a finely divided inorganic component to the paper stock after the final shear stage upstream of the headbox. However, it is also possible to use a procedure in which the retention aid is metered before the final shear stage upstream of the headbox and water-insoluble, uncrosslinked, organic polymers having an average particle size of less than 500 nm and a content of polymerized ionic monomers of less

than 1% by weight, alone or together with the finely divided inorganic component, are metered after the final shear stage upstream of the headbox.

- 5 In addition, combinations of a polymeric organic retention aid and those water-insoluble, uncrosslinked, organic microparticles having an average particle size of less than 500 nm and a content of polymerized ionic monomers of not more than 10% by weight which are obtainable by polymerizing the monomers in the presence of silica, waterglass, bentonite and/or mixtures thereof can be used in papermaking.
- 10 In a further embodiment of the novel process, water-insoluble, uncrosslinked, organic polymers having an average particle size of less than 500 nm and a content of polymerized ionic monomers of less than 1% by weight are used together with polymers of monoethylenically unsaturated carboxylic acids, for example
- 15 homopolymers of acrylic acid or methacrylic acid, copolymers of acrylic acid and methacrylic acid, copolymers of acrylic acid and maleic acid and/or copolymers of methacrylic acid and maleic acid. These polymers may if appropriate comprise further monomers, such as acrylamide and/or methacrylamide, incorporated in the form of polymerized units. The molecular weight  $M_w$  of this group of polymers is, for example, from 2 000 to 200 000, preferably in the range from 5 000 to 110 000. These polymers
- 20 result in an increase in the charge of the microparticles or preaggregation of the microparticles and hence improved retention in papermaking.

- According to a further process variant, the water-insoluble, uncrosslinked, organic polymers having a content of polymerized ionic monomers of less than 1% by weight
- 25 are used together with inorganic microparticles from the group consisting of bentonite, colloidal silica, sheet silicates and/or finely divided calcium carbonate. The particle size of said inorganic substances is, for example, from 1 to 100 000 nm, preferably from 5 to 500 nm. These particle size data are based in each case on the inorganic substances dispersed in water. For example, from 0.01 to 10, preferably from 0.05 to 2,
- 30 in particular from 0.1 to 1.2, parts by weight of at least one type of inorganic microparticles are used per part by weight of the organic microparticles. If organic microparticles containing up to not more than 10% by weight of monomers of group (c) are prepared by polymerizing the monomers in the presence of silica, waterglass and/or bentonite, corresponding amounts, based on the weight of the microparticles
- 35 formed, of inorganic microparticles are used in the polymerization.

- For example, bentonite, colloidal silica, silicates and/or calcium carbonate are suitable as the inorganic component of the microparticle system. Colloidal silica is to be understood as meaning those products which are based on silicates, e.g. silica
- 40 microgel, silica sol, polysilicates, aluminum silicates, borosilicates, polyborosilicates, clay or zeolites. Calcium carbonate may be used, for example, in the form of chalk, ground calcium carbonate or precipitated calcium carbonate as the inorganic



component of the microparticle system. Bentonite is understood generally as meaning sheet silicates which are swellable in water. These are in particular the clay mineral montmorillonite and similar clay minerals, such as nontronite, hectorite, saponite, sauconite, beidellite, alleverdite, illite, halloysite, attapulgite and sepiolite. These sheet silicates are preferably activated before they are used, i.e. converted into a form better swellable in water by treating the sheet silicates with an aqueous base, such as aqueous solutions of sodium hydroxide, potassium hydroxide, sodium carbonate or potassium carbonate. Bentonite in the form treated with sodium hydroxide solution is preferably used as the inorganic component of the microparticle system. The platelet diameter of the bentonite dispersed in water, in the form treated with sodium hydroxide solution, is, for example, from 1 to 2  $\mu\text{m}$ , and the thickness of the platelets is about 1 nm. Depending on the type and activation, the bentonite has a specific surface area of from 60 to 800  $\text{m}^2/\text{g}$ . Typical bentonites are described, for example, in EP-B-0235893. In the papermaking process, bentonite is added to the cellulose suspension typically in the form of an aqueous bentonite slurry. This bentonite slurry may comprise up to 10% by weight of bentonite. Usually, the slurries comprise about 3 – 5% by weight of bentonite.

Products from the group consisting of silicon-based particles, silica microgels, silica sols, aluminum silicates, borosilicates, polyborosilicates or zeolites may be used as colloidal silica. These have a specific surface area of 50 – 1 000  $\text{m}^2/\text{g}$  and an average particle size distribution of 1 – 250 nm, usually in the range 40 – 100 nm. The preparation of such components is described, for example, in EP-A-0041056, EP-A-0185068 and US-A-5176891.

Clay or kaolin is a water-containing aluminum silicate having a lamellar structure. The crystals have a layer structure and an aspect ratio (ratio of diameter to thickness) of up to 30:1. The particle size is such that at least 50% of the particles are smaller than 2 mm.

Carbonates, preferably calcium carbonate, used may be natural calcium carbonate (ground calcium carbonate, GCC) or precipitated calcium carbonate (PCC). GCC is prepared by milling and classification processes using milling assistants. It has a particle size such that 40 – 95% of the particles are smaller than 2 mm, and the specific surface area is in the range of 6 – 13  $\text{m}^2/\text{g}$ . PCC is prepared by passing carbon dioxide into calcium hydroxide solution. The average particle size is in the range of 0.03 – 0.6 mm, and the specific surface area can be greatly influenced by the choice of the precipitation conditions. It is in the range from 6 – 13  $\text{m}^2/\text{g}$ .

Papers having a particularly good strength are obtained by the novel process. The retention of fillers is improved compared with known processes.

Unless evident otherwise from the context, the stated percentages in the examples are always by weight. The molar masses of the polymers were determined by light scattering.

## 5 Examples

Test methods:

- Sheet formation  
10 Apparatus: Rapid-Köthen laboratory sheet former with accessories; testing according to DIN 54 358 Part 1 Production of laboratory sheets for physical tests = Rapid-Köthen method ISO 5269/2
- Ash retention: First Pass Ash Retention (FPAR)  
15 A dynamic drainage jar was brought to 900 rpm and then filled with 500 ml of stock suspension (8 g/l). After stirring for 10 seconds, x% of a polyacrylamide solution were added and stirring was effected for 20 seconds at 900 rpm and then reduced to 400 rpm. Thereafter, x%, based on stock, of the anionic  
20 flocculant component were added as dilute dispersion and stirring was effected for a further 15 seconds at 400 rpm. The dead volume of 25 ml was removed and discarded. 100 ml were collected in a volumetric flask and filtered with suction over a weighed Weissband filter. The filters were dried in a drying oven at 120°C, weighed, and ashed at 550°C. Depending on the filler composition, the filler  
25 content was calculated from the residue according to the following relationship

$$(1 - (\text{filler in the filtrate} / \text{filler in the sample})) \times 100$$

- Dry breaking length, wet breaking length:  
Apparatus: BXC-FR2.5TN.D09-002 from Zwick/Roell  
30
- Structural strength  
Apparatus: BXZ2.5/TS1S-006 from Zwick-Roell  
Tests according to DIN ISO 3 781

## 35 Starting materials

Cationic polymer A

Commercial cationic polyacrylamide having a molar mass of from 4 to 6 million and a solids content of 45% (Polymin® KE 2020 from BASF Aktiengesellschaft)

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Silica

Commercial colloidal silica having an average particle size of from 5 to 10 nm and a solids content of 10% by weight.

Bentonite

- 5 Commercial swellable clay of the montmorillonite type having a solids content of 90% and 10% of water (cf. US-A-4 306 781), obtainable under the trademark Mikrofloc® XFB from BASF Aktiengesellschaft

Fixing agent A

- 10 Commercial polyvinylamine having a molecular weight  $M_w$  of 250 000 and a solids content of 21%, obtainable under the name Catiofast® VFH from BASF Aktiengesellschaft

Anionic polymer A

- 15 Copolymer of acrylic acid and maleic acid having a molecular weight  $M_w$  of 70 000 and a solids content of 45%, obtainable under the name Sokalan® CP45 from BASF Aktiengesellschaft

Nanohybrids A

- 20 Mixture of polymer 1 and silica in the weight ratio 1 : 1

Solvitose® BPN

Cold-soluble starch having a solids content of 95%, obtainable from Avebe.

- 25 Preparation of polymers 1 to 4

Polymer 1

- 30 560 g of water and 633 g of a 15 percent strength by weight aqueous solution of aryl sulfonate were initially taken in a polymerization vessel, the solution was heated to 85°C and 50 g of a 7% strength aqueous sodium persulfate solution were then added.

- 35 The monomer mixture (feed 1) and the amount of initiator (feed 2) were then metered into the polymerization vessel via two separate feeds, beginning at the same time, in the course of 180 minutes, while maintaining the temperature.

After the end of the feeds, the 85°C were maintained for a further 30 minutes, and the reaction mixture was then cooled to room temperature. A pH of 4 was established with 3% strength aqueous sodium hydroxide solution.

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Feed 1:

245 g	Styrene
250 g	n-Butyl acrylate
3 g	Methacrylic acid

Feed 2:

1.5 g	Sodium persulfate
20 g	Demineralized water

- 10 The solids content of the dispersion was about 33%. The copolymer comprised 0.6% of methacrylic acid incorporated in the form of polymerized units. The light transmittance of a 0.01% strength solution was 99%. The weight average particle size d<sub>50</sub> was 61 nm. The pH of the dispersoin was 4.0 and the glass transition temperature T<sub>g</sub> of the polymer was 23°C.

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Polymer 2

- 800 g of a 2.5% strength Zeofloc® solution (J.M. Huber Corporation) and 253 g of a 15% strength aqueous solution of aryl sulfonate were initially taken in a polymerization vessel, the solution was heated to 85°C and 20 g of a 7% strength aqueous sodium persulfate solution were then added.

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- Thereafter, the monomer emulsion (feed 1) was added to the polymerization vessel in the course of 180 minutes and the initiator solution (feed 2) in the course of 195 minutes, via two separate feeds, beginning at the same time, while maintaining the temperature.

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- After the end of the feed, the 85°C were maintained for a further 30 minutes, and the reaction mixture was then cooled to room temperature and filtered over a filter having a mesh size of 45 µm. The pH was then brought to 4.0 by adding 3% strength aqueous sodium hydroxide.

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Feed 1:

100 g	n-Butyl acrylate
98 g	Styrene
1.9 g	Methacrylic acid

Feed 2:

1.0 g	Sodium persulfate
26 g	Demineralized water

- 5 The solids content of the dispersion was about 16%. The copolymer comprised 0.95% of methacrylic acid incorporated in the form of polymerized units. The weight average particle size  $d_{50}$  was 76 nm. The pH of the dispersion was 4.0 and the glass transition temperature  $T_g$  of the polymer was 31°C.

Polymer 3

- 10 300 g of water, 507 g of a 15% strength aqueous solution of aryl sulfonate, 12 g of methacrylic acid and 800 g of a 5% strength aqueous soda waterglass solution having a pH of 11.2 were initially taken in a polymerization vessel, the solution was heated to 85°C and 40 g of a 7% strength aqueous sodium persulfate solution were added.
- 15 Thereafter, the monomer mixture (feed 1) was added to the polymerization vessel in the course of 180 minutes and the initiator solution (feed 2) in the course of 210 minutes, via two separate feeds, beginning at the same time, while maintaining the temperature.
- 20 After the end of the feeds, the 85°C was maintained for a further 30 minutes and the dispersion formed was then cooled to room temperature and filtered over a filter having a mesh size of 400  $\mu\text{m}$ . The pH was then brought to 6.7 by adding 3% strength aqueous sodium hydroxide.

25 Feed 1:

176 g	Styrene
200 g	n-Butyl acrylate
12 g	Methacrylic acid

Feed 2:

40 g	Sodium persulfate solution (7% strength, aqueous)
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- 30 The solids content of the dispersion was about 25%. The copolymer comprised 3% of methacrylic acid incorporated in the form of polymerized units. The weight average particle size  $d_{50}$  was 68 nm. The pH of the dispersion was 6.7. The glass transition temperature  $T_g$  of the polymer was 21°C. The dispersion was divided. A 3% strength aqueous sodium hydroxide was then added to one part of the dispersion in an amount sufficient to bring the pH to 10.5. An aqueous dispersion having a solids content of
- 35 about 23.5% was obtained.

## Polymer 4

- 5 The other part of the aqueous dispersion of polymer 3, having a pH of 6.7, was brought to a pH of 10.5 by adding 5% strength aqueous soda waterglass solution. The solids content of the dispersion thus obtainable was 19.7%.

Examples 1 to 6, comparative examples 1 to 4

- 10 The efficiency of the polymers described above as retention aids was first tested on a stock model comprising a 70/30 pine sulfate/birch sulfate mixture with 70% Schopper Riegler 33 and 30% Schopper Riegler 70, 30% of Hydrocarb OG (based on pulp) and 0.6% of Solvitose® BPN (based on pulp) by the abovementioned test method. The pulp had in each case a consistency of 8 g/l and the pH of the pulp was 6.7. The type and amount of the starting material and the results are stated in tables 1 to 4.
- 15

Table 1

Examples	Amount*	Polymer	Amount*	Microparticles	FPAR [%]
Comparison 1	0.4	Cationic polymer A	1	Silica	68
Example 1	0.4	Cationic polymer A	1	Polymer 1	73

\* Amount added, kg of commercial product/t of paper

20

Table 2

Examples	Amount*	Polymer	Amount*	Microparticles	FPAR [%]
Comparison 2	0.4	Cationic polymer A	4	Bentonite	87
Example 2	0.4	Cationic polymer A	4	Polymer 1	89
Example 3	0.4	Cationic polymer A	4	Nanohybrid A	90

\* Amount added, kg of commercial product/t of paper

Table 3

Examples	Amount*	Polymer	Amount*	Microparticles	FPAR [%]
Comparison 3	0.4	Cationic polymer A	4	Bentonite	88
Example 4	0.4	Cationic polymer A	2	Polymer 2	91

\* Amount added, kg of commercial product/t of paper

5 Table 4

Examples	Amount*	Polymer	Amount*	Microparticles	FPAR [%]
Comparison 4	0.4	Cationic polymer A	3	Bentonite	90
Example 5	0.4	Cationic polymer A	3	Polymer 3	94
Example 6	0.4	Cationic polymer A	3	Polymer 4	96

\* Amount added, kg of commercial product/t of paper

Example 7 and comparative example 5

10

The stock model used was a wood-free paper stock having a consistency of 8 g/l and a pH of 6.7. 0.1%, based on dry paper stock, of fixing agent A (commercial product) was metered, the pulp was thoroughly mixed, the amounts of cationic polymer A and microparticles stated in table 5 were then added, thorough mixing of the components was ensured and the pulp was drained as described above. The results are shown in table 5.

15

Example 8

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Example 7 was repeated, except that the use of fixing agent A was dispensed with. The results are shown in table 5.

Table 5:

Examples	Amount*	Polymer	Amount*	Microparticles	FPAR [%]
Comparison 5	0.4	Cationic polymer A	3	Bentonite	88
Example 7	0.4	Cationic polymer A	3	Polymer 1	100
Example 8	0.4	Cationic polymer A	3	Polymer 1**	77

\* Amount added, kg of commercial product/t of paper

\*\* Without addition of fixing agent

#### 5 Example 9 and comparative example 6

The stock model used was a wood-free paper stock having a consistency of 8 g/l and a pH of 6.7. 1%, based on the amount of microparticles used, of anionic polymer A was added, the pulp was thoroughly mixed, the amounts of cationic polymer A and microparticles stated in table 6 were then added, thorough mixing of the components was ensured and the pulp was drained as described above. The results are shown in table 6.

#### Example 10 and comparative example 7

Example 9 was repeated, except that the use of anionic polymer A was dispensed with. The results are shown in table 6.

Table 6

Examples	Amount*	Polymer	Amount*	Microparticles	FPAR [%]
Comparison 6	0.4	Cationic polymer A	4	Bentonite	79
Comparison 7	0.4	Cationic polymer A	4	Bentonite**	83
Example 9	0.4	Cationic polymer A	4	Polymer 1	89
Example 10	0.4	Cationic polymer A	4	Polymer 1**	83

\* Amount added, kg of commercial product/t of paper

\*\* Without addition of Sokalan CP 45

#### Testing of the performance characteristics

500 ml of the stock suspension described above (consistency 8 g/l) were initially taken in a stirred vessel equipped with a propeller stirrer and was stirred at a speed of 900 revolutions per minute (rpm). After 10 seconds, a polyacrylamide solution (retention agent) was added, as in the testing of the ash retention, and stirring was



- effected for 20 seconds at 900 rpm and then at 400 rpm. Thereafter, the products stated in table 7 (bentonite and polymer 1) were metered in an amount of in each case 2 kg of commercial product per t of paper. Thereafter, the mixture was introduced into a Rapid-Köthen sheet former, and sheets having a basis weight of 80 g/m<sup>2</sup> were
- 5 produced. Dry and wet breaking length and the structural strength of the sheets were then determined by the methods described above. The results are shown in table 7.

Table 7

Paper test	Bentonite	Polymer 1
Dry breaking length [m]	3 442	4 298
Wet breaking length [m]	205	299
Structural strength [F max in N, z direction]	366	430

10 Example 11

Example 1 was repeated, except that 0.4 kg of commercial product of cationic polymer A per t of paper and 2 kg of polymer 1 per t of paper were used. The ash retention (FPAR) was 89%.

15

Comparative example 8

- Example 1 was repeated, except that 0.4 kg of commercial product of cationic polymer A per t of paper and 2 kg of an anionically emulsified styrene latex having a particle
- 20 size of 30 nm and a solids content of 33% were used. The ash retention (FPAR) was 81%.